

PROCESS FOR OPERATING A COMPRESSION IGNITION INTERNAL  
COMBUSTION ENGINE IN COMBINATION WITH A CATALYTIC  
REFORMER

Field of the Invention

The present invention relates to a process for operating a compression ignition internal combustion engine in combination with a catalytic partial oxidation reformer.

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Background of the Invention

Requirements to car exhaust emissions will be more and more stringent. Therefore, aftertreatment systems for exhaust gases from internal combustion engines have been developed.

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Spark ignition internal combustion engines can be operated at or close to stoichiometric fuel/air conditions. It is common to treat the exhaust gas of stoichiometric operated engines with a three-way conversion catalyst which promotes the oxidation of unburned hydrocarbons and carbon monoxide and the reduction of nitrogen oxides ( $\text{NO}_x$ ).

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In order to reduce particulate emissions and to improve efficiency, compression ignition internal combustion engines are typically operated at lean fuel/air conditions. Lean exhaust gas cannot be treated with a three-way conversion catalyst, since the presence of oxygen prevents the reduction of  $\text{NO}_x$ . Reducing the amount by which fuel injection timing is advanced from top dead centre can lead to a reduction in  $\text{NO}_x$  emission, but to an increase in particulate emission. Increasing the fuel injection advance will have the opposite effect

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- hence there is frequently observed to be a "trade-off" between NO<sub>x</sub> and particulate emission.

5 In order to reduce NO<sub>x</sub> emissions of lean burn internal combustion engines, NO<sub>x</sub> reducing exhaust gas treatment systems have been developed. These NO<sub>x</sub> reducing systems typically comprise a NO<sub>x</sub> reducing catalyst.

10 In US 5,412,946 for example, a NO<sub>x</sub> reducing catalyst comprising Pt on zeolite have been described. Such a catalyst promote the reduction of NO<sub>x</sub> to nitrogen in the presence of a reducing compound. It has been described in the art to use hydrocarbons, hydrogen or synthesis gas as reducing compound for this type NO<sub>x</sub> reducing catalyst.

15 NO<sub>x</sub> reducing systems that comprise both a deNO<sub>x</sub> catalyst and a NO<sub>x</sub> sorbent are also known in the art. For example from US 5,874,057, US 5,473,887 and WO 01/34950. During lean operation, NO<sub>x</sub> is absorbed from the exhaust gas; during richer operation, the sorbent is regenerated and the catalyst promotes reduction of NO<sub>x</sub> to nitrogen. It is disclosed that the exhaust gas can periodically be  
20 made richer (less oxygen) by adding fuel, hydrogen or synthesis gas to the lean exhaust gas.

25 An alternative method to reduce emissions of compression ignition internal combustion engines is by means of a process known in the art as fumigation. In a fumigation process, a gaseous fuel is mixed with the intake air of the engine prior to introducing the air/gaseous fuel mixture into the engine cylinder. Both diesel fuel and the air/gaseous fuel mixture are introduced into the engine. Known gaseous fuels for fumigation are for example natural gas, liquefied  
30 petroleum gas (LPG), and hydrogen gas.

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Another method for reducing emissions, especially NO<sub>x</sub>, in an internal combustion engine is by exhaust gas recirculation (EGR). NO<sub>x</sub> emissions are reduced with the increase of exhaust gas recirculation. A high level of recirculation, however, can result in poor combustion.

5 Various ways have been reported in the art by which recirculated exhaust gas may be enriched. In L.K.S Teo et al. "Hydrogen and Biodiesel Mixtures as Fuels for the Compression Ignition Engine" Proceedings of the THIESEL 10 2002 Conference on Thermo- and Fluid-Dynamic Processes in Diesel Engines, Birmingham, for example, the addition of hydrogen to recirculated exhaust gas has been described.

In order to ensure future emission limit values, especially for lean burn compression ignition internal 15 combustion engines, there is a need to further reduce emissions, in particular the emission of nitrogen oxides.

Summary of the Invention

It has now been found that, for compression ignition internal combustion engines, emissions can be further 20 reduced by using a fuel comprising a Fischer-Tropsch derived hydrocarbon stream as engine fuel in combination with the use of synthesis gas derived from a fuel comprising Fischer-Tropsch fuel for advanced aftertreatment of the exhaust gas and/or advanced 25 operation of the combustion engine.

Accordingly, the present invention relates to a process for operating a compression ignition internal combustion engine in combination with a catalytic partial oxidation reformer according to claim 1.

Brief Description of the Drawings

Different embodiments of the invention are described in detail and by way of example with reference to schematic Figures 1 to 4.

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Figure 1 shows a process according to the invention wherein synthesis gas is supplied to a NO<sub>x</sub> abatement system.

5 Figure 2 shows a process according to the invention wherein synthesis gas is supplied to the combustion chamber of the engine.

10 Figure 3 shows a process according to the invention wherein synthesis gas is supplied to the combustion chamber of the engine together with recirculated exhaust gas.

Figure 4 shows a process according to the invention wherein synthesis gas is supplied to both a NO<sub>x</sub> abatement system and a solid oxide fuel cell.

#### Detailed Description of the Invention

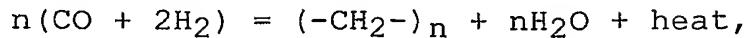
15 In the process according to the present invention, a compression ignition internal combustion engine is operated in combination with a catalytic partial oxidation reformer. Reference herein to a catalytic partial oxidation reformer is to a catalytic reaction zone for steam reforming, autothermal reforming or partial oxidation of a hydrocarbon fuel to form synthesis gas, i.e. a gas mixture containing hydrogen and carbon oxides. These reactions are described in more detail in the art, for example in Fuel Chemistry Division  
20 Reprints 2002, 47(2), 542.

25 The reformer produces synthesis gas that is used for operating the compression ignition internal combustion engine in such way that emissions are reduced.

30 Both the first fuel, i.e. the fuel for the engine, and the second fuel, i.e. the fuel for the reformer, comprise Fischer-Tropsch derived fuel. By "Fischer-Tropsch derived" is meant that the fuel is, or derives from, a synthesis product of a Fischer-Tropsch

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condensation process. The Fischer-Tropsch reaction converts carbon monoxide and hydrogen into longer chain, usually paraffinic, hydrocarbons :



5 in the presence of an appropriate catalyst and typically at elevated temperatures and/or pressures.

The fuel may be obtained directly from the Fischer-Tropsch reaction, or indirectly for instance by fractionation of a Fischer-Tropsch synthesis product or 10 from a hydrotreated Fischer-Tropsch synthesis product. Hydrotreatment can involve hydrocracking to adjust the boiling range (see, e.g. GB-B-2077289 and EP-A-0147873) and/or hydroisomerisation which can improve cold flow properties by increasing the proportion of branched 15 paraffins. EP-A-0583836 describes a two-step hydrotreatment process in which a Fischer-Tropsch synthesis product is firstly subjected to hydroconversion under conditions such that it undergoes substantially no 20 isomerisation or hydrocracking (this hydrogenates the olefinic and oxygen-containing components), and then at least part of the resultant product is hydroconverted under conditions such that hydrocracking and 25 isomerisation occur to yield a substantially paraffinic hydrocarbon fuel. The desired fuel fraction(s) may subsequently be isolated for instance by distillation.

Other post-synthesis treatments, such as polymerisation, alkylation, distillation, cracking-decarboxylation, isomerisation and hydroreforming, may be employed to modify the properties of Fischer-Tropsch 30 condensation products, as described for instance in US-A-4125566 and US-A-4478955.

Preferably, the same fuel is used for the engine and for the reformer, i.e. the first fuel and the second fuel

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are the same. This has the advantage that only one fuel storage tank is needed to provide fuel to both the engine and the reformer.

The use of Fischer-Tropsch derived fuel in a compression ignition internal combustion engine has several advantages. These fuels are highly paraffinic and thus have a high cetane number. Also, these fuels have a low sulphur content, thereby reducing the risk of sulphur poisoning of any catalytic system. Moreover, these fuels are inherently clean and thus result in lower emissions of particles (soot), NO<sub>x</sub>, hydrocarbons and carbon monoxide. Reference is made in this respect to R.H. Clark et al. "The Environmental Benefits of Shell GTL Diesel", *Proceedings of the 4<sup>th</sup> Int. Fuels Colloquium, 15-16 January 2003, Tech. Akad. Esslingen, Germany.*

It is known, for example from WO 99/19249, that Fischer-Tropsch derived fuels are very suitable fuels for catalytic reformers. An advantage of Fischer-Tropsch derived fuels over conventional internal combustion fuels in reformers is its cleanliness (no sulphur and reduced soot formation).

In order to benefit from these properties, both the first fuel and the second fuel comprise preferably at least 10% (v/v) of Fischer-Tropsch derived fuel, more preferably at least 50% (v/v), even more preferably at least 80% (v/v), still more preferably consist of Fischer-Tropsch derived fuel. It will be appreciated that the first fuel as such has to be suitable for compression ignition internal combustion engines. Thus, the first fuel has to meet the requirements for fuels for such engines, such as cetane number, flash point, total aromatics content, total sulphur content, as well as the specifications relating to the distillation curve and to

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the cold flow properties of the fuel. Therefore, the part  
of the first fuel that is not a Fischer-Tropsch derived  
fuel is preferably a diesel base fuel, such as petroleum  
derived gasoil, optionally in combination with oxygenates  
such as alcohols or fatty acid methyl esters and  
conventional diesel fuel additives. It has been found  
that less additives are needed in a fuel for a  
compression ignition internal combustion engine, if part  
of the fuel is a Fischer-Tropsch derived fuel. This  
implies that if the first and the second fuel are the  
same, the reformer is also fed with a fuel that has less  
additives as compared to a conventional diesel fuel. This  
is advantageous since some diesel additives could  
negatively affect the catalyst stability.

The Fischer-Tropsch derived fuel is preferably a  
gasoil, i.e. the fraction that is boiling in the gasoil  
boiling range.

In the process according to the invention, the engine  
exhaust emissions are further reduced by using synthesis  
gas for advanced aftertreatment and/or advanced engine  
operation. Such further reductions may be achieved by  
supplying synthesis gas to an exhaust gas aftertreater,  
for example a NO<sub>x</sub> abatement system, and/or to the  
combustion chamber of the engine.

The synthesis gas is produced in a catalytic partial  
oxidation reformer. The reaction that takes place in the  
reformer may be steam reforming, partial oxidation,  
autothermal reforming or a combination thereof. Suitable  
catalysts and reaction conditions for such reformers are  
known in the art. The fuel is reacted with water (steam  
reforming), oxygen (partial oxidation) or both  
(autothermal reforming or partial oxidation). Preferably,  
the reaction is partial oxidation or autothermal

reforming, since no external heat source is needed to maintain these reactions.

Air will typically be used as oxygen source for the reformer. Alternatively, exhaust gas from the engine may be used as source for oxygen and/or steam. If exhaust gas is used as steam source for the reformer, the exhaust gas may be introduced as such in the reformer or water may be condensed out of the exhaust gas before being introduced in the reformer.

In one aspect of the invention, exhaust gas of the engine (i.e. the part of the exhaust gas that is not recirculated to the combustion chamber of the engine and not fed to the reformer) is supplied to a NO<sub>x</sub> abatement system. At least part of the synthesis gas produced is also supplied to the NO<sub>x</sub> abatement system.

The NO<sub>x</sub> abatement system preferably comprises a NO<sub>x</sub> trap, which trap comprises a NO<sub>x</sub> reducing catalyst and a NO<sub>x</sub> sorbent. Such NO<sub>x</sub> traps are known in the art, for example from WO 01/34950 and US 5,473,887. A typical example of a suitable NO<sub>x</sub> trap is the combination of platinum on an alumina support as catalyst and barium oxide as sorbent. In one embodiment of the invention, the NO<sub>x</sub> abatement system comprises a single NO<sub>x</sub> trap. The NO<sub>x</sub> trap is continuously supplied with exhaust gas and intermittently supplied with synthesis gas. During the period that only exhaust gas is supplied to the NO<sub>x</sub> trap, NO<sub>x</sub> is absorbed on the sorbent, for example as Ba(NO<sub>3</sub>)<sub>2</sub> if the trap comprises a BaO sorbent. During the period that exhaust gas and synthesis gas are supplied to the NO<sub>x</sub> trap, the trap is regenerated and the catalyst promotes reduction of NO<sub>x</sub> to nitrogen.

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In another embodiment of the invention, the NO<sub>x</sub> abatement systems comprises two NO<sub>x</sub> traps as described hereinbefore. The two traps are operated in a so-called swing mode. One trap is supplied with exhaust gas and absorbs NO<sub>x</sub> (absorption mode) and the other trap is supplied with synthesis gas and desorbs NO<sub>x</sub> that is reduced to nitrogen (regeneration mode) and vice versa. Each trap is thus alternately supplied with exhaust gas and synthesis gas. An advantage of this swing mode operation as compared to the above-described operation of a single trap is that the regeneration is performed in the absence of oxygen, resulting in a more efficient regeneration.

A specific advantage of the use of Fischer-Tropsch derived fuel in both the engine and the reformer is that the fuel contains no sulphur and thus, the exhaust gas and the synthesis gas will contain less sulphur oxides. Sulphur oxides can strongly adsorb on a NO<sub>x</sub> trap and thus have a negative effect on the performance of such trap.

In still another embodiment, the NO<sub>x</sub> abatement system, comprises a NO<sub>x</sub> reducing catalyst without a NO<sub>x</sub> sorbent. Such NO<sub>x</sub> abatement systems are known in the art. Typically, such systems comprises a platinum supported on a zeolite. Exhaust gas and synthesis gas are simultaneously supplied to the catalyst. The catalyst promotes the reduction of NO<sub>x</sub> to nitrogen; the synthesis gas acts as reducing agent.

In a second aspect of the invention, at least part of the synthesis gas is supplied to the combustion chamber of the engine. In one embodiment (fumigation), synthesis gas is supplied to the combustion chamber by mixing it with the intake air prior to introducing the air to the

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combustion chamber. In an alternative embodiment (enriched EGR), synthesis gas is added to recirculated exhaust gas and together they are supplied to the combustion chamber.

5       In the fumigation embodiment, it may be necessary to ensure that the synthesis gas concentration in the intake air stream is below the flammability limit. Further, it will be appreciated that one should take care that the overall fuel-to-air ratio is optimised – wherein fuel is defined as first fuel plus synthesis gas supplied to the combustion chamber. Preferably, the amount of synthesis gas supplied to the combustion chamber of the engine is such that the volumetric ratio of synthesis gas-to-first fuel that is supplied to the combustion chamber is at most 25%, more preferably at most 20%.

10      If synthesis gas and recirculated exhaust gas are together supplied to the combustion chamber (enriched EGR), the volumetric ratio of 'combined synthesis gas plus exhaust gas' to 'first fuel' supplied to the combustion chamber is preferably at most 25%. The combined synthesis gas plus exhaust gas is usually admitted to the combustion chamber through a special valve.

15      The introduction of part of the synthesis gas into the combustion chamber (fumigation or enriched EGR)) may be combined with synthesis gas assisted aftertreatment, such as the above-described synthesis gas assisted NO<sub>x</sub> abatement.

20      In the process according to the invention, at least part of the synthesis gas produced is used for advanced aftertreatment or advanced engine operation. Additionally, part of the synthesis gas may be supplied to a fuel cell for electricity generation. In this way,

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it is possible to provide a vehicle with on-board electricity generation. The thus-obtained electricity may for example be applied for auxiliary power. e.g. for air conditioning, or for advanced valve control. The fuel cell is preferably a solid oxide fuel cell.

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#### Detailed Description of the Drawings

The invention is now illustrated by means of schematic drawings 1 to 4. Means for flow control, heat exchangers and other means for process control are not shown.

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In Figure 1 is shown a process for operating a compression ignition internal combustion engine 1 in combination with a catalytic partial oxidation reformer 2 and a NO<sub>x</sub> abatement system 3, wherein synthesis gas is supplied to NO<sub>x</sub> abatement system 3. Fuel (Fischer-Tropsch derived gasoil) from fuel storage tank 4 and air are supplied to engine 1 via lines 5 and 6, respectively. The fuel is vaporised and vaporised fuel and air are mixed before being combusted in the combustion chamber (not shown) of engine 1. Exhaust gas is discharged from the engine via line 7. Catalytic partial oxidation reformer 2 comprises a catalyst bed for partial oxidation. Fuel from storage tank 4 and air are supplied to reformer 2 via lines 8 and 9, respectively. Synthesis gas is produced and discharged from reformer 2 via line 10. NO<sub>x</sub> abatement system 3 comprises two NO<sub>x</sub> traps 11, 12. NO<sub>x</sub> trap 11 is supplied with the exhaust gas from line 7 via line 13 and valve 14. NO<sub>x</sub> trap 12 is supplied with the synthesis gas from line 10 via line 15 and valve 16. When the amount of NO<sub>x</sub> absorbed on NO<sub>x</sub> trap 11 has exceeded a certain limit, trap 11 is regenerated by supplying synthesis gas to it via line 17 and valve 18. During regeneration of NO<sub>x</sub>

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trap 11, NO<sub>x</sub> trap 12 is supplied with exhaust gas via line 19 and valve 20 for NO<sub>x</sub> absorption. Treated exhaust gas is discharged from NO<sub>x</sub> abatement system 3 via line 21.

5 In Figure 2 is shown a process for operating a compression ignition internal combustion engine 1 in combination with a catalytic partial oxidation reformer 2, wherein synthesis gas is supplied to the combustion chamber of engine 1. The synthesis gas that is  
10 discharged from reformer 2 via line 10 is added to the intake air of engine 1.

In Figure 3 is shown a process for operating a compression ignition internal combustion engine 1 in combination with a catalytic partial oxidation reformer 2, wherein synthesis gas and recirculated exhaust gas are together supplied to the combustion chamber of engine 1. A part of the exhaust gas discharged from engine 1 via line 7 is recirculated to the combustion chamber of engine 1 via line 22. The synthesis  
15 gas that is discharged from reformer 2 via line 10 is added to the recirculated exhaust gas in line 22.  
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In Figure 4 is shown a process for operating a compression ignition internal combustion engine 1 in combination with a catalytic partial oxidation reformer 2 and a NO<sub>x</sub> abatement system 3, wherein part of the  
25 synthesis gas is supplied to NO<sub>x</sub> abatement system 3 and part of the synthesis gas is supplied to solid oxide fuel cell 23. In this embodiment, only part of the synthesis gas discharged from reformer 2 via line 10 is supplied to NO<sub>x</sub> abatement system 3 via line 24. The remainder of the  
30 synthesis gas is led to the anode 25 of fuel cell 23 via line 26. Air is led to the cathode 27 of fuel cell 23 via line 28. The anode and cathode reactions of the fuel cell

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are allowed to take place and electricity is generated and fuel cell off-gas is discharged from the fuel cell via line 29.